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# 1 Introduction

There is a keen need for new forms of 'green' energy. The development of solar energy, such as that produced using photocatalysts, will have great long-term benefits since this form of energy is affordable, inexhaustible and clean. The most prevalently used photocatalyst, TiO<sub>2</sub>, is relatively inefficient, however, at utilizing visible light.<sup>1</sup> Numerous efforts to modify its band structure by doping have not been very successful because dopants usually act as recombination centers between the photogenerated electrons and holes, which markedly reduce the photocatalytic activity.<sup>2</sup>

As a potential substitute, WO<sub>3</sub>, which possesses a small band-gap energy of 2.4–2.8 eV, stable physicochemical properties and resilience to photocorrosion effects,<sup>3</sup> has strong photocatalytic activity in the visible-light region. However, its low conduction band level limits the photocatalyst to react with electron acceptors<sup>4</sup> and then increases the recombination of photogenerated electron-hole pairs. Thus, much effort has been focused on the particles modified with other components, such as Ag.<sup>5,6</sup>

# Synthesis of $WO_3 \cdot H_2O$ nanoparticles by pulsed plasma in liquid

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Pure orthorhombic-phase WO<sub>3</sub>·H<sub>2</sub>O nanoparticles with sizes of about 5 nm were synthesized by pulsed plasma in deionized water, in which tungsten electrodes provide the source of tungsten and the water is the source of oxygen and hydrogen. The quenching effect and liquid environment inherent in this pulsed plasma in liquid method resulted in ultra-small particles with lattice lengths (a = 5.2516 Å, b = 10.4345 Å, c = 5.1380 Å) larger than those of reference lattices. The emission lines of W I atoms, W II ions and H I atoms were observed by an optical emission spectrum in order to gather information on the synthetic mechanism. These nanoparticles showed higher absorption in the visible region than did ST-01 TiO<sub>2</sub> and Wako WO<sub>3</sub> nanoparticles. The WO<sub>3</sub>·H<sub>2</sub>O nanoparticles displayed more activity in the photocatalytic test than did the commercial TiO<sub>2</sub> sample (ST-01). Also, the absorption edge of WO<sub>3</sub>·H<sub>2</sub>O shifted to longer wavelengths in the UV-Vis absorption pattern relative to that of the anhydrous tungsten oxide.

Although less studied than anhydrous tungsten oxide, the association of water with tungsten oxide to form the  $WO_3 \cdot H_2O$  hydrate is considered to be important for the chemical properties of the resulting molecular species, and has been shown to cause a change in optical absorption.<sup>7</sup> This indicates that hydration may modify the band structures of  $WO_3$ , and thus may alter its photocatalytic properties for specific applications, even though the hydrate has lower photocatalytic efficiency than that of unhydrated  $WO_3$ .

In this study, we carried out and analyzed the results of a one-step synthesis of  $WO_3 \cdot H_2O$  nanoparticles, using the pulsed plasma in liquid method.<sup>8,9</sup>



**Fig. 1** Schematic of the system to generate pulsed plasma in deionized water by use of two tungsten electrodes.

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# 2 Experimental

As shown in Fig. 1, two metallic electrodes with a diameter of 5 mm and 99.95% tungsten purity (Rare Metallic Co., Ltd.) (hereafter called simply "tungsten electrodes") were submerged in degassed deionized water in a quartz beaker without adding conducting salts (pH value is about 7). Pulses with the same single-pulse duration of about 15 µs, as shown in Fig. 2, were generated between the two rod tips at a voltage of 100 V and current of 50 A when the electrolysis of water occurred. This process utilized deionized water as a source of oxygen and hydrogen, and tungsten electrodes as the source of tungsten. The whole synthetic system only contained the elements W, O and H (from tungsten rods and water) without contamination from other metal cations. The microsecond duration of pulsed plasma and the surrounding cool liquid helped to quench the growth of the small-sized nanoparticles. After a one-hour reaction, the yellow-green nanoparticles were carefully collected after drying in air at 120 °C for 2 hours.

Nanoparticle phase purity and structure were determined by X-ray diffraction (XRD) (Rigaku RINT 2000/PC) using Cu Ka radiation (40 kV, 200 mA). Crystal parameters were calculated by Rietveld refinement. Morphology and microstructural characterization of prepared samples were observed using high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai F20). The powders for HRTEM were prepared by putting them into ethanol and deaggregating them by sonication for 30 min. Optical emission spectra were obtained using an optical probe placed adjacent to the beaker, and data were transmitted via an optical fiber to an SEC2000-UV-VIS spectrometer. A HITACHI F-2500 luminescence spectrophotometer was used to evaluate photocatalytic activity by the photodecomposition of acetaldehyde into CO2. A Tedlar bag (AS ONE Co. Ltd.) was used as the photo-reactor vessel with a volume of 125 cm<sup>3</sup>. A mass of 100 mg of WO3 · H2O powder was spread evenly on the bottom of a glass dish (area: 9.6  $\text{cm}^2$  = irradiation area), which was placed in the reaction vessel described above. Five hundred ppm of acetaldehyde was prepared in the vessel by injection of saturated gaseous acetaldehyde. Irradiation was conducted at room temperature after equilibrium between the gaseous and adsorbed acetaldehyde had been reached, which was ascertained by monitoring the concentration by a gas chromatograph approximately every 30 minutes. Methane and CO byproducts were negligible. The excited light source was an LED lamp with the parameters of 455 nm and 1 mW m<sup>-2</sup> at room temperature. The photocatalytic results were compared with a commercial TiO<sub>2</sub> nanoparticle (ST-01, anatase, Ishihara Sangyo Kaisha, Ltd.) and commercial WO<sub>3</sub> (Wako Pure Chemical Industries, Ltd.). UV-Vis spectra of the synthesized sample, ST-01 and Wako WO<sub>3</sub> were taken using a JASCO V-550 UV/VIS spectrometer.

# 3 Results and discussion

#### 3.1. Characterization of WO3 · H2O nanoparticles

The crystal structure of the sample was checked by XRD (Fig. 3). The crystal yielded diffraction peaks at  $2\theta = 16.5$ , 19.3, 23.8, 25.7, 30.5, 33.4, 34.2, 35.0, 37.7, 38.9, 42.8, 45.9, 49.2, 52.8, 54.3, 56.3, 62.8 and  $66.2^{\circ}$ , corresponding well with the JCPDS card number 43-0679. This diffraction confirmed that the obtained nanoparticles were the WO<sub>3</sub>·H<sub>2</sub>O hydrate. The absence of metallic tungsten indicated the high purity of the WO<sub>3</sub>·H<sub>2</sub>O nanoparticles synthesized by the pulsed plasma in liquid method.

Table 1 lists Rietveld refinement parameters of  $WO_3 \cdot H_2O$ obtained by pulsed plasma in deionized water, comparing them with Szymanski's data<sup>10</sup> and reference data in PDF# 43-0679. The crystallographic structure of the synthesized  $WO_3 \cdot H_2O$  sample is well refined in the orthorhombic *Pnmb* space group (see Fig. 4 and 5) in the region of 14 to 90 degrees. Observed data are indicated by dots, and the calculated profile is indicated by a solid line. Short vertical bars below the pattern represent the positions of all possible Bragg reflections, and the line below the short vertical bars represents the difference between the observed and calculated patterns. Because the hydrogen atoms are very light, they were neglected and not calculated in this



Fig. 2 Plot of current *versus* time for a single-pulse duration generated by the pulsed plasma in liquid system.



Fig. 3 XRD powder pattern of  $\mathsf{WO}_3{\cdot}\mathsf{H}_2\mathsf{O}$  nanoparticles by pulsed plasma in deionized water.

Table 1	Structure parameters of WO3·H2O nanoparticles compared
with Szy	manski's and PDF#43-0679 data

Sample	Plasma sample	Szymanski's data <sup>8</sup>	PDF#43-0679
Space group	Pnmb	Pnmb	Pnmb
Lattice parame	eter		
a (Å)	5.2516(8)	5.249(2)	5.238
b (Å)	10.7345(1)	10.711(5)	10.704
c (Å)	5.1380(7)	5.133(2)	5.12
W			
Position	4c	4c	4c
x	0.25	0.25	
у	0.2228(2)	0.2209(8)	
z	0.0123(2)	-0.0037(3)	
01			
Position	4c	4c	4c
x	0.25	0.25	
у	0.4293(2)	0.436(2)	
z	0.0620(9)	0.075(4)	
02			
Position	4c	4c	4c
x	0.25	0.25	
у	0.0680(2)	0.066(2)	
z	-0.0578(9)	-0.064(4)	
03			
Position	8d	8d	8d
x	0.4626(8)	0.495(8)	
ν	0.2555(3)	0.227(2)	
z	0.2864(9)	0.249(5)	
T overall	0.046758		
Profile R facto	ors		
GOF	1.72		
Rp	14.52		
<i>R</i> <sub>wp</sub>	18.32		







Fig. 5 The crystal structure model of  $\mathsf{WO}_3\!\cdot\!\mathsf{H}_2\mathsf{O}$  nanoparticles by pulsed plasma in deionized water.

refinement, and were just added into the model of the structure for creating the image. Compared with the cell parameters from the other sources, the crystal parameters of the  $WO_3 \cdot H_2O$ nanoparticles prepared by pulsed plasma in deionized water are the largest. In our experiment, the plasma was produced in liquid, and water was the only source of oxygen. It was highly possible that the synthesized nanocrystals contain oxygen vacancies which tend to increase the lattice lengths.<sup>11</sup> The quenching effect by the surrounding cool liquid during plasma synthesis may also help to inhibit the crystal growth and result in lattice expansion of the nanocrystals.<sup>12</sup> Furthermore, the atomic positions are shifted a little in the plasma sample (Table 1), which indicates that the pulsed plasma in liquid method can introduce structural distortion in the synthesized nanoparticles.

High energy-density plasma commonly increases the synthesis temperature, leading to nanoparticle growth, but low energy-density plasma reduces the production rate. Thus, to optimize the balance between them, experimental parameters such as single-pulse duration and voltage were adjusted in order to prepare uniform small-sized WO3·H2O nanoparticles in large amounts. Besides, the synthetic environment of the pulsed plasma in liquid method helps to disperse nanoparticles in the liquid. As shown in Fig. 6, the morphology and particle size were investigated by HRTEM. The images indicated that very small orthorhombic WO3·H2O nanoparticles with sizes of about 5 nm were obtained by pulsed plasma in deionized water. The calculated size according to the Scherer equation from the peaks of the XRD patterns was about 250 um. Because we dried the particles before carrying out the XRD experiments, the results here are considered to be due to the aggregation of particles. The crystal parameters of WO3 · H2O according to PDF card #43-0679 are 5.238 Å imes 10.704 Å imes 5.12 Å (90.0 imes 90.0 imes90.0). As shown for the example in Fig. 6a, some particles were only about 1-2 nm in diameter, and contained only 1 or 2 unit cells. We conclude that some nanoparticles were nearly as small as the unit cell.13

Fig. 7 shows the energy-dispersive X-ray spectroscopy (EDX) pattern of a plasma sample, in which the element Cu is due to the HRTEM grid and the carbon peak source is the membrane



Fig. 6 High-resolution TEM images of WO\_3·H\_2O nanoparticles by pulsed plasma in deionized water. (a) Image of a WO\_3·H\_2O crystal with an ultra-small size.



Fig. 7 EDX pattern of the  $WO_3 \cdot H_2O$  nanoparticles synthesized by pulsed plasma in deionized water and shown in the HRTEM image. Inset shows a table of the percentage content of the elements W and O in these nanoparticles.

covering the Cu grid. There were no other contaminating elements. The atomic percentages of W and O were 21.06% and 78.93%, respectively, closely fitting with the ratio of these two elements in  $WO_3 \cdot H_2O$ , which is equal to 1:4.

#### 3.2. Mechanism of formation

The optical emission spectrum of the pulsed plasma during the experiment is shown in Fig. 8. The spectral lines were identified using reference data. The coexistence of atoms W I, ions W II, and atoms H I, apparent from the optical emission spectrum, allows elucidation of the mechanism of formation of the  $WO_3 \cdot H_2O$  nanoparticles as follows: it is assumed that, first, very hot plasma with extreme energy ablates the tungsten metal in the tips of the rods to form very active tungsten atoms W I; simultaneously, the deionized water is decomposed by plasma into oxygen and



Fig. 8 Optical emission spectrum of the pulsed plasma in deionized water with tungsten electrodes.

hydrogen. Soon after, the atoms W I in the plasma discharge zone lose electrons and transform into ions W II, which then react with oxygen and hydrogen to quickly form a  $WO_3 \cdot H_2O$ molecular complex. When these complexes aggregate into crystallites and are quenched suddenly by the surrounding cool liquid, ultra-small  $WO_3 \cdot H_2O$  nanoparticles appear. According to the Balmer series, there should be additional emission lines due to H atoms, but these lines at about 410 nm, 430 nm, 490 nm, are masked by the strong emission peaks of W atoms.

#### 3.3. Photocatalytic properties and UV absorption

Photocatalytic properties of pure tungsten hydrate has not been garnering much attention. In the published literature, most of the reported hydrates were mixed with other components such as WO<sub>3</sub> and Ag,<sup>6,14</sup> and the hydrates that were investigated were usually in the forms WO<sub>3</sub>·0.33H<sub>2</sub>O and WO<sub>3</sub>·0.5H<sub>2</sub>O.<sup>15-17</sup> Only recently, Q. Zeng et al.18 reported the photocatalytic properties of pure WO3·H2O hollow spheres. However, the synthesized spheres only showed high photocatalytic efficiency in acid solutions. Fig. 9 shows the dependence of the CO<sub>2</sub> evolution rate on the decomposition of acetaldehyde under visible-light irradiation over pure WO3·H2O samples synthesized by pulsed plasma method. The irradiated wavelength was controlled by using various cut-off filters. The photocatalytic activity of WO<sub>3</sub>·H<sub>2</sub>O nanoparticles irradiated by visible light at 455 nm was higher than the photocatalytic activity of commercial TiO<sub>2</sub> samples (ST-01) under any conditions. After 720 min, the amount of CO<sub>2</sub> generated from the plasma sample is about 28.4% larger than that from ST-01.

In order to explain the photocatalytic behavior of  $WO_3 \cdot H_2O$ nanoparticles made using plasma and compare their light absorption ability to that of ST-01 and of commercial Wako  $WO_3$ , UV-Vis absorption spectra (Fig. 10) were measured for these three species. The obvious red shift of the absorption edge and higher absorbance of the  $WO_3 \cdot H_2O$  sample in the visiblelight region, compared with that of the ST-01 TiO<sub>2</sub> sample,



Fig. 9 Photocatalytic properties of  $WO_3 \cdot H_2O$  nanocrystals grown in deionized water by pulsed plasma, compared with that of a commercial TiO<sub>2</sub> nanoparticle (ST-01).



Fig. 10 UV-Vis absorption spectra of  $WO_3 \cdot H_2O$  nanoparticles synthesized by pulsed plasma in deionized water compared with that of a commercial TiO<sub>2</sub> nanoparticle (ST-01) and of commercial  $WO_3$  (Wako).

indicate the higher absorption and better photocatalytic properties of the  $WO_3 \cdot H_2O$  sample. Furthermore, the shift in the absorption edge from about 440 nm for anhydrous tungsten oxide to near 480 nm for the  $WO_3 \cdot H_2O$  sample shows that the band structure can be modified by hydration.

### 4 Conclusion

Pure  $WO_3 \cdot H_2O$  nanoparticles were prepared in a one-step synthesis by a pulsed plasma in deionized water method using two tungsten rods. The lattice of the sample was expanded relative to those of references, perhaps due to the quenching effect by the surrounding cool liquid during the preparation and the in-liquid environment for the synthesis. The mechanism of formation of the WO<sub>3</sub>·H<sub>2</sub>O particles was analyzed using an emission spectrum. These nanoparticles, with the ultra-small particle size of about 5 nm, exhibit higher absorption than do TiO<sub>2</sub> (ST-01) and Wako WO<sub>3</sub>. The red shift of the absorption edge in the UV-Vis absorption pattern of the plasma-synthesized sample, compared with the absorption edge of the anhydrous tungsten oxide, indicates the possible band modification and the potential applications of WO<sub>3</sub>·H<sub>2</sub>O nanoparticles in the solar energy field.

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